

Article

# Removing Gaseous NH3 Using Biochar as an Adsorbent

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Abstract: Ammonia is a major fugitive gas emitted from livestock operations and fertilization production. This study tested the potential of various biochars in removing gaseous ammonia via adsorption processes. Gaseous ammonia adsorption capacities of various biochars made from wood shaving and chicken litter with different thermal conditions and activation techniques were determined using laboratory adsorption column tests. Ammonia adsorption capacities of non-activated biochars ranged from 0.15 to 5.09 mg·N/g, which were comparable to that of other commercial activated carbon and natural zeolite. There were no significant differences in ammonia adsorption capacities of steam activated and non-activated biochars even if the surface areas of the steam activated biochars were about two orders of magnitude greater than that of non-activated biochars. In contrast, phosphoric acid activation greatly increased the biochar ammonia adsorption capacity. This suggests that the surface area of biochar did not readily control gaseous NH<sub>3</sub> adsorption. Ammonia adsorption capacities were more or less linearly increased with acidic oxygen surface groups of non-activated and steam-activated biochars. Phosphoric acid bound to the acid activated biochars is suspected to contribute to the exceptionally high ammonia adsorption capacity. The sorption capacities of virgin and water-washed biochar samples were

Keywords: gaseous ammonia; biochar; adsorption; activation; regeneration

## 1. Introduction

Ammonia is a colorless gas with a pungent odor, explosive when mixed with air in certain proportions, and irritating to the eyes, nose, and throat at less than 50 ppm. Ammonia emissions from livestock operations and fertilizer production account for about 90% of total ammonia emissions in the USA [1]. Activated carbon, alumina, silica gel, and zeolite have been used to remove gaseous ammonia from the gas streams in the ammonia manufacturing process [2]. In general, gaseous ammonia is removed by adsorption. In the literature, gaseous ammonia sorption capacities of commercial activated carbon range from 0.6 to 4.7 mg/g [3–5]. The ammonia sorption capacity of activated carbon increased to 17.5 mg/g after oxidation treatment with HNO<sub>3</sub> [4]. Equilibrium ammonia sorption capacities of natural zeolites were less than 6.3 mg/g [7]. Another potential adsorbent for gaseous ammonia removal may be biochar, a carbonaceous byproduct of pyrolysis of plant and animal manure feedstocks.

Biochar along with combustible gases and oils is produced when biomass feedstock is subjected to pyrolysis, an anaerobic thermal decomposition process. Pyrolysis temperature, heating rates, and biomass feedstock compositions and properties influence the product distribution and properties [8–11]. Researchers reported multiple benefits of applying biochar to soil such as improving carbon sequestration, soil fertility, and reduction of greenhouse gas emissions from soil [11,12]. Another beneficial use of biochar may be as an adsorbent for removal of gaseous ammonia. Conducting passive adsorption isotherm experiments with biochar and ammonia in Tedlar bags or sealed jars researchers reported that biochar was able to remove ammonia [13–16]. An average adsorption capacity of 6.7 mg/g was determined from experiments in which woody biochars were exposed to ammonia in sealed jars for a week [14]. When a gaseous ammonia was forced to pass through a biochar column with a residence time less than 1 s, the sorption capacity of biochars made from peanut hull and palm oil shell were lower than that from the above passive conditions [17].

Although above studies demonstrated the potential for removing gaseous ammonia using biochar, none of these addressed an important issue of regenerating spent biochar saturated with ammonia. Typically steam has been used to regenerate spent activated carbon; however, it requires high capital and energy expenditures. Because ammonia is highly soluble in water (about 310 g/L at 25 °C [18]), this study explores the feasibility of using water to regenerate the biochar. This paper reports the results of gaseous ammonia removal experiments using a laboratory-scale continuous-flow biochar adsorption column system. The results include some unique physico-chemical characteristics and ammonia sorption

capacities of 30 different water-washed and non-washed, activated and non-activated biochar samples made from wood shavings and chicken litter under different thermal conditions and activation methods.

## 2. Materials and Methods

## 2.1. Biochar

Biochars were prepared from softwood shavings (WS) and chicken litter (CL). The raw material has been pyrolyzed at two temperatures: WS at 250 °C and 500 °C with residence times of 1.3 min and 1.8 min, respectively; and whereas 1.5 min and 2.1 min residence times were used for CL at 250 °C and 480 °C, respectively. The biochar samples were ground using a mechanical grinder and sieved. Particles between sizes 0.5–2 mm were used in sorption studies and activation.

## 2.2. Activation of Biochar

Steam activation involved injecting water into a nitrogen gas flow (1.6 L/min) entering the heated retort. Biochars were activated at 800 °C for 45 min, at 3 mL/min water flow rate. Acid activation involved soaking biochar samples in 30% (w/w) phosphoric acid overnight. Samples were placed in the retort, heated to 450 °C under breathing air, and activation was done under air for 60 min. More detailed activation procedure can be found elsewhere [19].

### 2.3. Sample Handling/Preparation/Designation

The biochar samples were tested in 3 different conditions. First, samples were tested "as-received (AR)" in which the biochars were placed in a desiccator cabinet overnight before being used in the adsorption tests. Second, the biochars were washed using deionized water at ratio of 0.1 g char to 5 mL water. The biochar and water were combined in a beaker which was placed on the shaker overnight. The next day, the pH was measured for each sample. The water was then removed and the biochar was placed in an oven at 100 °C for drying overnight. The sample was then removed from the oven and placed in the desiccator cabinet for cooling. This washed char was then tested as "virgin-washed (VW)". After the biochars were used in the adsorption tests, the spent biochars were washed using the same washing procedure as above and then labeled as "used-washed (US)". These handling procedures were used for both non-activated and activated biochars.

A sample identification system of xx-yyyyy-zz was used to designate different biochar samples (Table 1). The first two letters indicated activation status; non-activated (NA), steam-activated (SA), or phosphoric acid-activated (AA) biochar samples. Next 5 letter and number combinations indicated feedstock material and pyrolysis temperature. For wood shavings (WS) biochar samples prepared at 250 °C or 500 °C were designated as xx-WS250-zz or xx-WS500-zz, respectively. Similarly, chicken litter (CL) biochar samples prepared at 250 °C or 480 °C were designated as xx-CL250-zz or xx-CL480-zz, respectively. The last two letters indicated whether the biochar samples were as-received (AR), virgin-washed (VW) or used-washed (US).

Symbols	Feedstock	<b>Pyrolysis</b> Temperature	Activation	<b>Tested Condition</b>
NA-WS500-AR	Wood Shaving	500 °C	None	As Received
SA-WS500-AR	Wood Shaving	500 °C	Steam	As Received
AA-WS500-AR	Wood Shaving	500 °C	Acid	As Received
NA-WS500-VW	Wood Shaving	500 °C	None	Virgin Washed
SA-WS500-VW	Wood Shaving	500 °C	Steam	Virgin Washed
AA-WS500-VW	Wood Shaving	500 °C	Acid	Virgin Washed
NA-WS500-US	Wood Shaving	500 °C	None	Used Washed
SA-WS500-US	Wood Shaving	500 °C	Steam	Used Washed
AA-WS500-US	Wood Shaving	500 °C	Acid	Used Washed
NA-WS250-AR	Wood Shaving	250 °C	None	As Received
SA-WS250-AR	Wood Shaving	250 °C	Steam	As Received
AA-WS250-AR	Wood Shaving	250 °C	Acid	As Received
NA-WS250-VW	Wood Shaving	250 °C	None	Virgin Washed
SA-WS250-VW	Wood Shaving	250 °C	Steam	Virgin Washed
AA-WS250-VW	Wood Shaving	250 °C	Acid	Virgin Washed
NA-WS250-US	Wood Shaving	250 °C	None	Used Washed
SA-WS250-US	Wood Shaving	250 °C	Steam	Used Washed
AA-WS250-US	Wood Shaving	250 °C	Acid	Used Washed
NA-CL480-AR	Wood Shaving	480 °C	None	As Received
SA-CL480-AR	Wood Shaving	480 °C	Steam	As Received
NA-CL480-VW	Wood Shaving	480 °C	None	Virgin Washed
SA-CL480-VW	Wood Shaving	480 °C	Steam	Virgin Washed
NA-CL480-US	Wood Shaving	480 °C	None	Used Washed
SA-CL480-US	Wood Shaving	480 °C	Steam	Used Washed
NA-CL250-AR	Wood Shaving	250 °C	None	As Received
SA-CL250-AR	Wood Shaving	250 °C	Steam	As Received
NA-CL250-VW	Wood Shaving	250 °C	None	Virgin Washed
SA-CL250-VW	Wood Shaving	250 °C	Steam	Virgin Washed
NA-CL250-US	Wood Shaving	250 °C	None	Used Washed
SA-CL250-US	Wood Shaving	250 °C	Steam	Used Washed

Table 1. Biochar samples tested for adsorption experiments.

## 2.4. Adsorption Tests

Adsorption experiments were conducted by passing NH<sub>3</sub> standard gas (National Welders, Florence, SC, USA, 20 or 103 ppm  $\pm$  1% to 2%) through a column of biochar at a rate of 3 L/min (Figure 1). The NH<sub>3</sub> concentration of the effluent gas was measured using the photoacoustic multi-gas monitor (Innova 1412, California Analytical Instruments, Inc., Orange, CA, USA). The pressure drop across the column (Alnor micromanometer, Huntington Beach, CA, USA) as well as the temperature and relative humidity (Omegaette, Stamford, CT, USA) of the effluent gas were also measured. The average relative humidity of gas stream was 2.93%  $\pm$  0.57%. The sample column consisted of a capped PVC nipple with a hose fitting at each end. The bottom of the column was filled with 6 mm glass beads. A piece of filter paper was placed on top of the glass beads to prevent the biochar from entering the bottom of the column. The column was then filled with 1.01 to 14.10 g biochar. The filled column was placed on a ring stand

and Teflon<sup>™</sup> tubing was connected to the inlet and outlet of the column. Ultra-pure nitrogen gas was then introduced into the column at a rate of 3 L/min. The column was flushed with nitrogen gas until the effluent measured by the photoacoustic reached equilibrium of approximately zero ammonia. The effluent gas usually reached equilibrium of zero after about 15 min. The photoacoustic gas analyzer was flushed with nitrogen gas prior to the flushing of the column. After the column was sufficiently flushed, a known concentration of NH<sub>3</sub> gas was introduced into the column at a rate of 3 L/min.

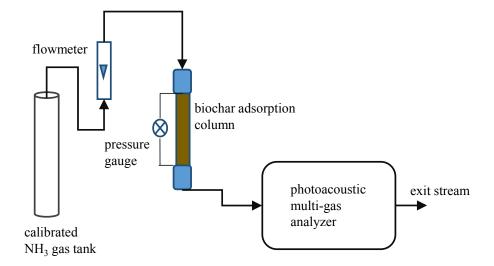
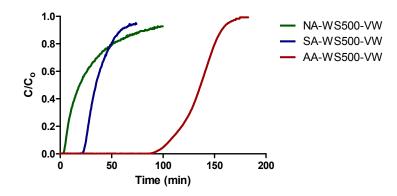


Figure 1. Sorption column experimental setup.

The effluent NH<sub>3</sub> concentration was measured continuously until the end of the test run. Figure 2 shows typical breakthrough curves by plotting the ratios of effluent to influent ammonia concentrations (C/C<sub>o</sub>). At the end of each test, the column was removed and the photoacoustic analyzer along with the inlet/outlet tubing were flushed with nitrogen. Two sizes of columns were used for the adsorption tests. A 2.5 cm diameter PVC nipple was used for non-activated biochars and a 1.3 cm diameter nipple was used for the various activated biochars. The control ammonia adsorption capacities without biochar were 0.13  $\pm$  0.01 and 0.09  $\pm$  0.02 mg-NH<sub>3</sub>-N for the 2.5 cm diameter column and the 1.3 cm diameter column setups, respectively. All adsorption experiments were conducted at room temperature (21.6  $\pm$  1.8 °C).



**Figure 2.** Typical breakthrough curves (about 3 g of non-activated and steam-activated biochars with 20 ppm influent NH<sub>3</sub> concentration; 1.8 g of acid-activated biochar with 103 ppm influent NH<sub>3</sub> concentration).

#### 2.5. Adsorption Capacity Estimation

Ammonia adsorption capacity of the biochar packed filter was determined with the bed depth service time (BDST) model [20–23]. Bohart and Adams (1920) first proposed the original BDST model relating filter bed depth to the service time taken for breakthrough to occur [14]. Hutchins (1973) later simplified the original BDST model equation and proposed a linear relationship between service time and filter bed depth [16] (Equation (1)).

$$t = \frac{zq_{vo}}{uC_o} - \frac{1}{kC_o} \ln\left(\frac{C_o}{C} - 1\right) \tag{1}$$

where  $C_o$  = influent solute concentration (mg NH<sub>3</sub>-N m<sup>-3</sup>); C = effluent solute concentration (mg NH<sub>3</sub>-N m<sup>-3</sup>); k = kinetic coefficient (m<sup>3</sup>·min<sup>-1</sup>·mg<sup>-1</sup> NH<sub>3</sub>-N);  $q_{vo}$  = maximum volumetric adsorption capacity (mg NH<sub>3</sub>-N m<sup>-3</sup>); t = service time (min); u = superficial velocity (m·min<sup>-1</sup>); z = filter depth (m).

The maximum biochar adsorption capacity  $(q_{vo})$  was then estimated from the intersection  $(\frac{zq_{vo}}{uC_o})$  of a regression line (fitted to Equation (1)) obtained by plotting t vs.  $\ln \left(\frac{C_o}{C} - 1\right)$ .

## 2.6. Intrinsic and Bulk Density and Surface Area Measurements

Intrinsic or "skeleton" density was measured with a Quantachrome multipycnometer Model "MVP-6DC" using ultra high purity (UHP) helium. Measurements were made using the micro-sample cell (~4 mL). Each sample was flushed with helium for at least 10 min prior to measurement. Measurements were made by filling the reference cell to 117.2 kPa; then opening the sample cell which lowered the pressure to ~41.4 kPa. The readings were taken after allowing the pressure to stabilize for 2 min. A minimum of 3 readings were made. Density measurements were made for "as received" char samples.

Bulk density was calculated by filling a 10-mL graduated cylinder with biochars and recording the sample weight. A minimum of 3 readings were made for each biochar. Surface area of the biochar was measured using Quantachrome Nova 2200 (Boynton Beach, FL, USA). The surface area (SA-N<sub>2</sub>) was determined by the Brunaer-Emment-Teller (BET) equation with multipoint adsorption isotherms of N<sub>2</sub> at 77 K.

#### 2.7. Temperature Programmed Decomposition Analyses

Temperature programmed decompositions (TPD) were performed on a Quantachrome ASiQ with an attached Pfeiffer Vacuum PrismaPlus mass spectrometer (Quantachrome Instruments, Boynton Beach, FL, USA). In a typical TPD analysis, about 100 mg of sample were placed in a sample tube sandwiched between packings of quartz wool, dried, and degassed at 120 °C under vacuum for 20 min. Helium (ILMO gas, Jacksonville, IL, USA) flow was then started at a flow rate of 40 mL/min and the cell purged for 20 min prior to the start of the measurement. The TPD measurement used a heating ramp at 10 °C/min to 1000 °C. The mass spectrometer outputs of m/z 28 (CO), and 44 (CO<sub>2</sub>) were recorded. The decomposition of Ca(C<sub>2</sub>O<sub>4</sub>)·H<sub>2</sub>O (Alfa Aesar, Ward Hill, PA, USA) was used as a gas standard.

## 2.8. Statistics

Statistical results included means, standard deviations, analysis of variance (ANOVA), *t* test, and least significant difference at a 0.05 probability level (LSD<sub>0.05</sub>) for multiple paired comparisons among means using statistical software GraphPad Prism (GraphPad Software, Inc., La Jolla, CA, USA).

## 3. Results and Discussion

## 3.1. Biochar Characteristics

Table 2 shows the bulk and intrinsic density and surface area of both activated and non-activated biochars. While the biochar bulk densities ranged from 0.15 to 0.28 g/cm<sup>3</sup>, the intrinsic biochar densities were about one order of magnitude higher (1.33 to 2.22 g/cm<sup>3</sup>). The intrinsic densities of non-activated biochars were comparable to that of wood and grass biochars (1.344 to 1.742 g/cm<sup>3</sup>) as reported in the literature [24]. Activation further increased the intrinsic density to 2.22 g/cm<sup>3</sup>. This increase in intrinsic density was attributed to the increase in inner pore volume within the biochar particle while maintaining fixed carbon and inorganic components. As a result, the total surface area also increased with the increase in intrinsic density. Activation increased both intrinsic density and the surface area of the biochars. The surface areas of activated biochars increased more than two orders of magnitude compared to that of non-activated biochars.

Biochar	Bulk Density (g/cm <sup>3</sup> )	Intrinsic Density (g/cm <sup>3</sup> )	Surface Area (m <sup>2</sup> /g)
NA-WS500-AR	$0.23\pm0.01$	$1.33\pm0.05$	$0.88\pm0.07$
SA-WS500-AR	$0.22 \pm 0.00$	$1.99\pm0.07$	$511 \pm 1.4$
AA-WS500-AR	$0.20\pm0.00$	$1.85 \pm 0.08$	$538\pm3.9$
NA-WS250-AR	$0.22\pm0.00$	$1.44 \pm 0.03$	$0.61 \pm 0.12$
SA-WS250-AR	$0.19\pm0.00$	$1.97 \pm 0.04$	$573 \pm 15$
AA-WS250-AR	$0.15 \pm 0.01$	$1.80 \pm 0.03$	$851 \pm 7$
NA-CL480-AR	$0.28\pm0.00$	$1.70 \pm 0.07$	$4.50\pm0.24$
SA-CL480-AR	$0.28\pm0.01$	$1.97 \pm 0.03$	$420\pm40$
NA-CL250-AR	$0.24 \pm 0.01$	$1.55 \pm 0.01$	$1.40 \pm 0.11$
SA-CL250-AR	$0.21 \pm 0.01$	$2.22 \pm 0.01$	$592\pm0.93$
LSD <sub>0.05</sub>	0.01	0.08	25

**Table 2.** Bulk and intrinsic density and surface area of biochar samples.

 $LSD_{0.05}$  = least significant difference value for comparison of any two means within the same column.

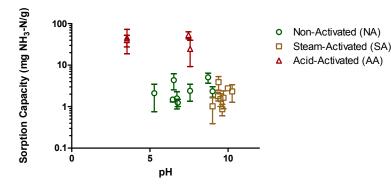
## 3.2. Ammonia Sorption Capacity of Biochar

The maximum ammonia sorption capacities of both activated and non-activated biochars are shown in Table 3 and Figure 3. Ammonia adsorption capacities for non-activated biochars ranged from 0.15 to  $5.09 \text{ mg} \cdot \text{N/g}$ , which were comparable to 0.6 mg $\cdot \text{N/g}$  dry granular activated carbon [3]. Steam activated biochars did not show any improvement in their sorption capacity although the surface area increased more than two orders of magnitude. It indicates that the surface area did not control gaseous NH<sub>3</sub> adsorption. On the contrary, activating biochars with phosphoric acid greatly increased the ammonia sorption capacity to more than an order of magnitude. This increase in sorption capacity may be attributed to the change in biochar surface charge and decrease in pH resulting from activation. For example, the total surface charge of NA-WS500-AR decreased slightly from 0.37 to 0.00 meq H<sup>+</sup>/g from steam activation, whereas it increased dramatically to 2.11 meq H<sup>+</sup>/g from acid activation [19]. The pH of WS500 (VW) increased from 5.3 to 9.6 after steam activation, but decreased to 3.5 after acid activation (Table 4). However, when ammonia adsorption capacities of all biochar samples were plotted against their pH, it did not appear to have any correlation between them (Figure 3).

Biochar	As-Received (AR)	Virgin-Washed (VW)	Used-Washed (US)	LSD <sub>0.05</sub>
NA-WS500	$0.84\pm0.10$	$1.25 \pm 0.25$	$2.41 \pm 1.06$	1.26
SA-WS500	$0.63\pm0.45$	$1.64 \pm 0.75$	$1.79\pm0.42$	1.12
AA-WS500	$31.49 \pm 16.11$	$40.11 \pm 12.61$	$24.57 \pm 15.33$	29.50
NA-WS250	$2.47 \pm 1.25$	$2.11 \pm 1.36$	$4.36 \pm 1.82$	2.99
SA-WS250	$0.53 \pm 0.31$	$0.87\pm0.27$	$1.02 \pm 0.63$	0.87
AA-WS250	$51.86 \pm 24.11$	$45.82 \pm 26.99$	$53.09 \pm 10.15$	45.36
NA-CL480	$1.19\pm0.03$	$2.35 \pm 0.67$	$5.07 \pm 1.38$	1.77
SA-CL480	$0.44\pm0.48$	$2.77 \pm 0.16$	$1.52 \pm 0.51$	0.83
NA-CL250	$0.14 \pm 0.21$	$1.48 \pm 0.19$	$1.58 \pm 0.70$	0.87
SA-CL250	$0.20 \pm 0.14$	$2.33 \pm 1.05$	$3.90 \pm 1.43$	2.06
LSD <sub>0.05</sub>	15.64	16.09	10.05	-

Table 3. Ammonia adsorption capacities of biochar samples (mg-NH<sub>3</sub>-N/g-biochar).

LSD<sub>0.05</sub>, least significant difference value for comparison of any two means within the same row or column.



**Figure 3.** Ammonia sorption capacity *vs.* pH of non-activated, steam- and acid-activated biochars (error bar = 1 SD).

Biochar	Virgin-Washed (VW)	Used-Washed (US)	<sup>†</sup> Significantly Different ( <i>p</i> < 0.05)?
NA-WS500	$6.78\pm0.10$	$7.57\pm0.55$	Y
SA-WS500	9.71	$9.36 \pm 1.25$	-
AA-WS500	$3.53\pm0.20$	$7.58 \pm 1.27$	Y
NA-WS250	$5.28\pm0.05$	$6.53\pm0.53$	Y
SA-WS250	$9.63\pm0.90$	$9.01\pm0.67$	Ν
AA-WS250	$3.54\pm0.18$	$7.47\pm0.29$	Y
NA-CL480	$9.01 \pm 1.06$	$8.72\pm0.78$	Ν

**Table 4.** pH of biochar samples before and after ammonia sorption.

Biochar	Virgin-Washed (VW)	Used-Washed (US)	<sup>†</sup> Significantly Different ( <i>p</i> < 0.05)?
SA-CL480	9.09	$9.51 \pm 1.42$	-
NA-CL250	$6.46\pm0.25$	$6.73\pm0.31$	Ν
SA-CL250	$10.26 \pm 1.60$	$9.39 \pm 1.22$	Ν

 Table 4. Cont.

<sup>†</sup> Unpaired *t*-test with Welch's correction.

To further elucidate biochar surface functionalities on ammonia sorption capacity, biochar samplers were characterized by TPD. During the TPD, the oxygen-containing functionalities can be characterized by the temperature at which CO and CO<sub>2</sub> evolve. Thermally labile acidic oxygen surface groups such as carboxylates decompose to CO2 at moderately low temperatures near 300 °C followed by anhydrides and lactones at temperatures reaching 800 °C. CO evolves from the decomposition of anhydrides, phenols at 600 °C, and carbonyls from ketones and quinones at temperatures reaching 900 °C [25]. The results from the TPD analyses of our biochar samples are shown in Table 5. These samples further pyrolyzed during the analyses resulting in tar deposits on the sample tube, making gas analysis unreliable. As a result, the samples pyrolyzed at lower temperatures could not be analyzed by TPD. The biochars prepared from wood shavings were lower in acidic surface oxygen groups than the biochars prepared from chicken litter. As observed by Goncalves [4], the ammonia adsorption capacity positively correlated to acidic surface oxygen groups (represented by mmol CO<sub>2</sub> evolved per g of biochar in Figure 4). The exception being the phosphoric acid activated wood shavings. These samples show a slight increase in CO<sub>2</sub> evolution but the ammonia adsorption exceeds what would be expected from acid-base binding at the organic acid sites. The higher binding capacity of these biochars may be attributed to phosphoric acid bound to the biochar.

In order to evaluate the potential of using water to regenerate the spent biochar, the ammonia sorption capacities of virgin-washed and used-washed biochars were compared (Table 3). Except for the CL480, the sorption capacities of virgin and regenerated biochars were not statistically different. The results suggest that the spent biochar can be conveniently regenerated with water. When compared to the as-received biochars, the ammonia sorption capacities of the virgin-washed chicken litter biochars increased slightly (Table 3). It was suspected that washing the biochars might have increased the access to pore sites that might have been blocked by excess mineral content and/or washing with deionized water might have removed ions from biochar surface contributing to the basicity.

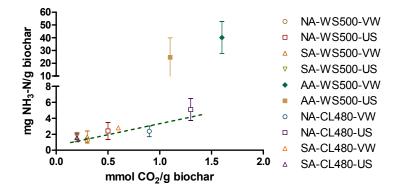


Figure 4. Dependence of the ammonia sorption capacity as a function of the amount of acidic oxygen surface groups (error bar = 1 SD).

Biochars	CO (mmol/g Biochar)	CO <sub>2</sub> (mmol/g Biochar)	mg-NH <sub>3</sub> -N/g-Biochar
NA-WS500-VW	1.2	0.3	1.25
NA-WS500-US	1.6	0.5	2.41
SA-WS500-VW	0.3	0.3	1.67
SA-WS500-US	0.7	0.2	1.83
AA-WS500-VW	5.0	1.6	40.15
AA-WS500-US	3.6	1.1	24.62
NA-CL480-VW	2.0	0.9	2.37
NA-CL480-US	3.1	1.3	5.09
SA-CL480-VW	1.6	0.6	2.80
SA-CL480-US	1.1	0.2	1.56

**Table 5.** Total amount of CO<sub>2</sub> and CO groups evolved in the temperature programmed decompositions (TPD) experiment.

## 4. Conclusions

Gaseous ammonia adsorption capacities of various biochars made from different feedstocks (wood shaving and chicken litter), thermal conditions (250 °C, 480 °C, and 500 °C), and activation techniques (steam vs. acid activation) were determined using laboratory adsorption column tests. Bulk densities of these biochars ranged from 0.15 to 0.28 g/cm<sup>3</sup> while the intrinsic (skeleton) densities ranged from 1.33 to 2.22 g/cm<sup>3</sup>. The surface area of biochar dramatically increased after activation (both steam and phosphoric acid activation techniques) from less than 5 to more than 500 m<sup>2</sup>/g. Ammonia adsorption capacities of non-activated biochars ranged from 0.15 to 5.09 mg·N/g. These adsorption capacities were comparable to that of other commercial activated carbon and natural zeolite. While steam activating the biochars did not improve its sorption capacity even with two orders of magnitude increase in surface area, phosphoric acid activation greatly increased the sorption capacity. This suggested that the surface area of biochar did not really control gaseous NH3 adsorption. Except with phosphoric acid activated biochars, ammonia adsorption capacities were more or less linearly related to increases in acidic oxygen surface groups. This suggests that the amount of evolved CO<sub>2</sub> determined from TPD could be used to predict biochar's NH<sub>3</sub> adsorption capacity. We suspected that phosphoric acid bound to the acid activated biochars contributed to the exceptionally high ammonia adsorption capacity. The sorption capacities of virgin and water-washed biochar samples were not different, suggesting the potential of regenerating spent biochar simply with water. The results of this study suggest that non-activated biochars can replace commercial activated carbon in removing gaseous ammonia and the removal efficiency will greatly increase with phosphoric acid activation.

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## **Author Contributions**

Kyoung Ro, Isabel Lima, and Guidqopuram Reddy originally conceived and designed the experiments; Kyoung Ro, Isabel Lima, and Michael Jackson conducted experiments; Bin Gao analyzed the data. All fully participated in interpreting the data and writing the manuscript.

# **Conflicts of Interest**

The authors declare no conflict of interest.

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